1 2 CO₂-ENRICHED, LOW, AND VERY LOW, VAPOR PRESSURE LIQUID HYDROCARBON FUELS 3 4 5 6 TECHNICAL FIELD 7 8 This invention pertains generally to the physical composition formed by 9 the combination of carbon dioxide (CO2) absorbed in liquid hydrocarbon fuels having low, and very low vapor pressures. The invention includes fuels used in 10 11 12 12 13 14 15 16 17 18 19 fuel-powered engines and devices, such as: diesel and jet aircraft engines, fuel-oil burning devices such as domestic and commercial heating systems, or electrical power generation facilities, and resid-oil burning engines such as those used in large cargo ships. **BACKGROUND OF THE INVENTION** More particularly, the present invention is a CO2-enriched, low, or very low, vapor pressure hydrocarbon fuel having objectives and advantages that are 20 important to the fuel industry, to the environment, and to fuel economics. The 21 present invention: 22 provides improved combustion characteristics; a.) 23 promotes fuel micro-droplet production; b.) 24 reduces exhaust soot particulate; c.) 25 d.) reduces exhaust carcinogens; may be effective in reducing the infrared 'footprint' of the exhaust of 26 e.) 27 military aircraft and vehicles; de-oxygenates fuel (including at NTP) during the CO2/fuel mixing 28 f.) 29 process; provides a means to reduce the complexity and cost of fuel tank inerting 30 g.)

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systems;

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- h.) provides a cost-effective interim emissions-reducing technology for existing engines that can readily be implemented, particularly in cities having high atmospheric soot particulate;
- i.) provides potential tax credit relief to fuel companies for accelerated ground-based vehicle and aircraft soot particulate reductions;
- j.) provides a means to reduce fuel viscosity (when desired);
- k.) may be effective in cleaning fuel-injection systems;
- 1.) may be effective in improving fuel economy;
- m.) which, through improved fuel economy may provide a net reduction in CO2 production (CO2 in exhaust / per gallon);
 - n.) which, through improved fuel economy may provide a cost-savings in fuel-use which is near, equal to, or greater than, the combined cost of CO2, CO2-enriched fuel / technology licensing, and systems / equipment used for fuel tank ullage inerting;
 - o.) which can utilize an industrial CO2 that is recovered (re-cycled) from industrial stacks and vents
 - p.) provides new enhanced fuel transferring and storing safety;
 - q.) acts as a 'self-inerting fuel';
 - r.) uses fuel as a 'weightless container' for transferring and storing substantial volumes of CO2;
 - s.) provides a new means for safely extending Jet-A fuel supplies by mixing in percentages of JP-4 or naphthas into CO2-enriched Jet-A (e.g. during fuel shortages, fuel embargoes, or in times of national security if Jet-A supply needs to be increased, for example, during war, or other international crisis).
 - t.) provides a sufficient volume of CO2 in fuel (including at NTP) such that the CO2 will serve as an inerting medium in the ullages of fuel tanks to which such fuel is transferred and stored, or where such gas is extracted from fuel derived from such tanks and is immediately, or is stored and subsequently, directed back into that fuel tank's ullage;
 - u.) is transferrable and storable in, existing fuel distribution systems / equipment such as those used at airports and other re-fueling terminals;

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DESCRIPTION OF THE RELEVANT ART

Reference:

Jones, Minor C, K, 2,303,950

Ginsbrugh et al, 6,293, 525 B1

Search of prior art has not revealed any patents having the combination of the CO2 and liquid hydrocarbon fuels as specified in the present invention, or having a type of gas-fuel that would be transferable or storable in existing fuel distribution infrastructures; fuel delivery systems, vehicles and equipment, or in standard fuel tanks found in diesel trucks, aircraft, ground-based vehicles, and ocean-going vessels or; the tanks used for supplying heating devices or at power-generation facilities. The search also did not reveal the above-mentioned actual and potential benefits of the present invention, such as an ullage-combustion suppressive 'self-inerting fuel'; a means to improve combustion and/or fuel economy; a means to promote reduced fuel-droplet size (sometimes referred to as fuel "micro-droplets"); or a means, through reduced fuel-droplet size, to reduce soot particulate emissions and carcinogens in the exhaust of liquid hydrocarbon fuel-powered engines or devices, because the smaller droplets more often burn to extinction quicker.

For reference purposes, the search did find Jones, which teaches the mixing of carbon dioxide in an aviation gasoline (a positive vapor pressure hydrocarbon fuel with added volatile fuel ends) where Jones processes the fuel and /or maintaines it with additional physical apparatus in an unconventional manner. For example, the aviation gasoline of the Jone's patent must first go through physical apparatus comprising a vacuum-inducing means. This apparatus is required to produce and sustain a negative atmospheric condition in a baffled vertical fuel mixing tank (a vacuum-maintaining tank) in order to first promote the removal of absorbed oxygen from Jones' aviation gasoline. Immediately following the oxygen removal stage, CO2 is added to replace it. It should also be noted that the Jones' patent seeks several results that, due to fuel chemistry changes in years following the expiration of the patent, are no longer needed in, or attainable with, contemporary commercial grades of fuel. Furthermore, putting positive vapor pressure fuel in a

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vacuum state will pull out lighter ends (such as butane) from the fuel, which will adversely affect fuel performance. Continued exposure to a vacuum will remove the middle range of hydrocarbon molecules and ultimately the heavier range of molecules.

The Jones patent intent was a vacuum removal of one gas and provide positive pressure (greater than 1 atmosphere) for placement and maintenance of another gas (CO2), a means to remove oxygen from fuel that might otherwise degas into the vapor space (ullages) of aircraft fuel tanks containing the Jones'-processed aviation gasoline.

By contrast, the composition of the present invention can be achieved with gasfuel mixing at NTP (normal temperature and pressure) i.e. without negative and positive pressure mixing stages and uses the CO2 as an inerting medium. It is also noted that contemporary aviation gasoline now contain anti-oxidants that are inexpensive and do not require the fuel vacuum and pressurization stages needed to process the Jones' fuel. Whereas this invention is based upon hydrocarbon fuel having contemporary needs which it satisfies..

CO2 solubility in contemporary grades of hydrocarbon fuels, show that CO2 concentrations in the range Jones specifies would require constant positivepressure (if not hi-pressure) storage and handling conditions. Thus, the only way to maintain Jones' 100%-300% concentrations of CO2 in modern aviation gasoline would be to make, transfer, distribute, and store, the fuel continuously under impractical (or as Jones says "super atmospheric") pressures. It is widely known that virtually all fuel tanks of diesel trucks, aircraft and other groundbased vehicles, are vented to allow for expansions and contractions of fuel-tank ullages caused by altitude and temperature changes, and by fuel usage. Thus, it would be necessary to retrofit all such vehicles with unvented pressure-capable tanks in order to store aviation gasoline having the Jones' concentrations of CO2 (up to and including the "five atmospheres" he specifies). This goal would be especially challenging in that a commercial aircraft will typically experience a change of four atmospheres in the various phases of a single flight (which is why their tanks must be vented). It would also be necessary to have specially equipped fuel transportation vehicles for the delivery of Jones' pressurized gasoline.

Such prerequisites to the processing, transferring, transportation, handling, and use of Jones' aviation gasoline again, are evidence that Jones did not achieve a practical physical composition patent, especially as it pertains to contemporary technology. Rather, the Jones' physical composition can only exist with the employment of unconventional physical apparatus that in the contemporary fuel market are not only unnecessary, they would require a costly re-building of entire fuel distribution and storing systems.

By contrast, the present invention provides gas-fuel mixtures with fuels other than gasoline (hydrocarbon fuels with low, and very low, vapor pressures at NTP), where such mixtures are attainable and/or storable at NTP having effective concentrations of CO2 that provide new fuel safety-enhancing and improved combustion advantages. These advantages are achieved without Jones' hipressure transportation, handling and storage conditions.

Lastly, the Jones patent decribes a safety-enhancing aspect of his fuel, which, assuming the gas concentrations he specifies were attainable, is intended to reduce the danger of fuel fires in the event of catastrophic fuel tank ruptures. For example, the Jones' fuel is described as being advantageous during aircraft crashes, or during fuel tank ruptures caused by bullets piercing the tanks in times of war. In contrast, the practicably attained physical composition of the present invention is comprised of CO2-enrichment of low, or very low, vapor pressure fuels, whose safety-enhancing characteristics are only intended to inert the contents of the ullages of fuel tanks that are intact (i.e. non-ruptured).

SUMMARY OF THE INVENTION

Vehicles and devices that burn low, and very low, vapor pressure hydrocarbon fuels have been in use for over a century and the chemistry compositon of such fuels (including relatively newer jet fuels) have largely remained the same since their commercialization. While such fuels offer a potent source of power to the respective engines or devices that utilize them, they also have drawbacks that the physical composition of the present invention can help to reduce. For instance, it has recently been declared by the California State Air

Quality Board that the black soot emissions that emanate from a diesel engine (used in cars, trucks, heavy equipment, trains, ships and the like), and the soot from jet turbines, are carcinogenic. Thus, practicably attainable fuel technology, which improves diesel and jet fuel combustion, particularly during its acceleration phase (highest emission emitting phase), and otherwise reduces such emissions, provides an important and timely solution to this environmental and health-related concern. Recent tests conducted with California State-Approved Infrared Test Equipment concluded that the improved fuel of the present invention reduces harmful emissions by as much as 60% during repeatable accelerations on an unmodified diesel engine when using an optimum and/or controllable concentration of CO2 absorbed within Diesel #2 fuel. Further testing using a standardized EPA test produced similar reductions in soot.

Alternatively, by controlling concentrations of CO2 absorbed within low vapor pressure hydrocarbon fuels, the physical composition of the present invention is also effective in enhancing the safety of the fuel when it is stored in storage receptacles, whether such receptacles are stationary or reside in any one or more of a variety of liquid hydrocarbon fuel-powered vehicles. For instance, hydrocarbon-based fuels can evaporate fuel into a vapor space, or ullage, of the fuel receptacle in which they reside. These evaporated vapors are usually low molecular weight hydrocarbons which mix with the air in the ullage, and under certain conditions have proven to be dangerously explosive. Even JP-4 (a military aircraft fuel which is mostly kerosene with some low molecular weight naphtha) usually has a flammable ullage above the fuel and this volatile chemical condition has had deadly consequences. FAA experts have concluded that the mid-air explosion of TWA FLT 800 out of New York was due to flammable vapors which were emitted from relatively heated Jet-A fuel located in the plane's center fuel tank.

Enhanced safety in the storing and/or transporting of these fuels can be achieved by reducing the amount of air which can enter, or otherwise reside above the fuel of such fuel tanks by displacing or replacing the air with an inert gas concentration that will no longer support combustion. For example, approximately 40% or greater concentration of CO2 will effectively suppress fuel

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ullage-combustibility under most operating conditions. The CO2-enriched hydrocarbon fuels of the present invention provide this desirable combustionsuppressive condition in two ways. In the first method, the concentration of inertgas residing in a particular fuel exceeds that fuel's equilibrium CO2/fuel state and consequently degasses excess CO2 from the fuel under known conditions, such as: the passage of time, increases in temperature, agitation of the fuel, and/or a change in relative pressure-such as the ascent of a commercial aircraft to a crusing altitude. In this first method, CO2-enriched fuel can be transferred to a fuel tank such that a known excess concentration of CO2 degasses from the fuel during re-fueling; for example when the fuel tank is only being partially filled with fuel (and the excess degassed CO2 serves to inert the ullage above the fuel level). In the second method, CO2-enriched fuel is pumped from the fuel tank and a gas-scavenging stage of the pump extracts CO2 from the fuel and the extracted CO2 is either directed back into the same fuel tank (e.g. its ullage), or is stored in one or more CO2 storage receptacles for subsequent fuel tank inerting purposes (as described in co-pending patents). In either case, the intended equilibrium state can deliberately be exceeded (without the vacuum stage described in the Jones patent). For example, CO2 can be mixed in the fuel under controllable positive pressures or under such pressures with agitation (as described in co-pending patents), in which case the fuel is still transferable and storable in conventional fuel delivery systems, and the excess gas will subsequently degas at predictable rates and/or volumes. For example, an aircraft having a shorter duration flight could be fueled with a CO2-enriched Jet-A fuel having a gas-to-liquid ratio of CO2 that is absorbed at a substantially higher ratio, that is achieved by employing a higher mixing pressure of the CO2 in the liquid fuel, to promote faster degassing than with fuel which is mixed at lower, or ambient, pressures (suitable for longer flights).

It is also noted, that in consideration of the environment, the quantity of CO2 necessary to inert a commercial aircraft, such as a Boeing 747 flight of 6.5 hours and a distance of 3000 nautical miles, is equal to the amount of CO2 emitted during just a few seconds of engine exhaust from the flight. Furthermore, the present invention includes the mixing of a commercial grade of CO2 that has

been recovered (re-cycled) from high-CO2-content industrial stacks and vents. Moreover, standardized EPA testing, exhaust pyrometer testing, and engine RPM analysis have each indicated that improved fuel performance may be caused by the CO2-enriched fuels of the present invention (the improved fuel economy being caused by the CO2 reducing fuel droplet size, and/or by a cleaning of fuel injection components). For a frame of reference: each one half percent improvement in fuel economy would reduce the 747's 3000 mile flight output of CO2 by 2200 pounds (this is several times the amount of CO2 needed to inert the fuel tanks during the entire flight, and thus, would represent a net reduction in CO2 production).

Thus practicably attained CO2-enriched liquid hydrocarbon fuels are provided which overcome significant shortcomings of gas-fuel mixtures requiring special processing, handling, and unconventional physical apparatus, and which achieve an enhanced safety fuel, as well as an improved combustion fuel, and do so using inexpensive (and optionally recycled) CO2.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 shows a graph of the volume of "Carbon Dioxide" (CO2) that can be mixed, or absorbed, in a volume of low vapor pressure liquid hydrocarbon fuels, namely "JP-4 / Jet-B", "JP-8 / Jet-A", "JP-7", and "JP-5".

FIGURE 2 is a diagrammatical depiction of a barrel of crude oil illustrating the hydrocarbon fuel constituents of the barrel, and ranges of fuel in the barrel representing "Low, and Very Low, Vapor Pressure Fuels", "High Vapor Pressure Fuels", "Jet-A1 or JP-8", "JP-3", "JP-4", and "JP-5".

DETAILED DESCRIPTION OF THE INVENTION

The graph in FIG. 1 plots volume ratio and depicts a range of the volume of CO2 that can be mixed, or absorbed, in a volume of low vapor pressure liquid hydrocarbon fuels, namely "Diesel, JP-4 / Jet-B", "JP-8 / Jet-A", "JP-7", and "JP-

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5 and shows that as temperature goes up the volume ratio of the CO2 within the fuels goes down. For example, at -20°C about 1.7 volumes of CO2 can be absorbed in one volume of JP1- Jet-A. At just under 50°C an approximate 1:1 ratio of gas to fuel is possible. Commercial vehicle and aircraft fuels such as diesel#2 and Jet-A have a similar composition and consequently similar absorption ratios of gas to fuel are possible.

Several physical factors are known to change the ratio of inert-gas which is mixable in, and/or retainable within, a particular type of low, or very low, vapor pressure liquid hydrocarbon fuel; the CO2 gas is physically absorbed without reacting chemically with the fuel. These factors can be controlled, or predicted, and in numerous instances require no additional physical structure, or equipment, in order to occur. These factors include: temperature change, pressure differential, agitation, time, and, convection of the mixed or mixing fuel. Thus, a factor such as a known temperature change during a mixing phase, or during a degassing phase, will have predictable results which can be advantageously used. For example, cooler CO2-enriched liquid hydrocarbon fuel may be stored in relatively cooler underground tanks, with the knowledge that as the fuel becomes warmer it will degas faster at a known rate. Similarly, agitation during a mixing phase or during a degassing phase will have predictable results. For instance, after refueling a vehicle or aircraft will encounter fuel agitation as it rolls over the natural series of bumps such as one encounters on roads (car), or during a 40 second or so takeoff roll (commercial aircraft). Alternatively, a pressure differential can be exploited to accelerate gas absorption in, and/or desorption from, fuels, as mentioned previously in the case of aircrafts having different flight durations. Time is also a known factor that can be used advantageously to predict absorption or desorption rates, including rates when also affected by any of the above-mentioned factors that can change the ratio of the physical composition. Or CO2-enriched fuel can be made with a gas/fuel ratio that remains fairly stable through all phases of a flight (i.e. through all changes in altitude).

In the case of the physical composition being used as a vapor combustionsuppression fuel, it can be beneficial to mix CO2 in fuels such as diesel #2 or Jet-A in a ratio that exceeds the fuel's equilibrium state of the gas/fuel mixture (such

as that exceeding the 50% ratio previously mentioned). For example, a 1.5:1 gas/fuel ratio might be employed where 0.75 of a fuel's CO2 volume is meant to degas from the fuel under relatively ambient conditions, and more CO2 can degas, or be extracted from the fuel, according to one or more of the factors or methods previously mentioned. Since an ullage in a tank containing a typical hydrocarbon-based fuel can be inerted by containing approximately 35% or more volume of CO2 therein, it can be seen that a sufficient volume of inert-gas can be retained within the fuel to in effect act as a "self-inerting-fuel".

In the case of the application of these physical compositions providing an improved combustion and/or emission-reducing fuel, it can be beneficial to mix the CO2 with the hydrocarbon fuel in less than 1:1 to 3:1 gas/liquid ratio of CO2 to fuel (e.g. a range from 0.1:1 to 1:1) gas/fuel ratios in the approximate range of 15-25% that have been shown to reduce harmful particular emissions in diesel #2 fuel by as much as 60%. The various CO2/fuel ratios may indicate that minute inert-gas bubbles can form in 'micro-droplets', and upon reaching the surface of the droplet can disperse the droplets into smaller ones which creates a larger mixing surface for fuel and air molecules for optimized dispersion of the fuel which results in improved (and more complete) combustion in an engine or fuel-burning device. This benefit may be of further advantage during cold weather, or during cold-engine starting.

Additionally, liquid fuel convection is a means of replacing surface fuel molecules so that they may absorb CO2 molecules from a blanket of CO2 gas above the liquid surface. Thus, the factors of convection and time, or convection and fuel temperature and/or CO2 temperature, or other factors mentioned above can be predictable and used advantageously to attain desired CO2/fuel concentrations and results. Without the surface layer of CO2 the same methods create degassing of the CO2...

Because a CO2-enriched low vapor pressure fuel can be easily and practicably attained by a number of controllable methods, with the outcome being a CO2/fuel mixture that is transferrable and storable in existing fuel distribution systems, the present invention provides a fuel that can be easily made at a number of junctures in the fuel distribution system. For instance, at an airport fuel farm, at

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any one or more of a variety of re-fueling terminals, in underground storage tanks, on fuel tankers, fuel barges, on a ship, and the like.

Figure 2 shows a diagrammatical depiction of a barrel of crude oil illustrating the hydrocarbon fuel constituents of the barrel. Ranges of fuel in the barrel representing low vapor pressure fuels are bracketed, and those representing high vapor pressure fuels are separately bracketed. It can also be seen in Fig. 2 that Jet-A1 or JP-8 can be derived from 10% of the crude, JP-3 from 50% of the crude, JP-4 from 25% of the crude, and JP-5 from 2% of the crude. An important benefit of the present invention pertains to fuel supply, particularly during a national emergency such as a fuel shortage caused by any one of a number of factors, such as an international crisis, a war, a fuel embargo, or an international trust type of control over the supply / cost of fuels. In any such instance, for example a shortness of supply in Jet-A fuel could threaten national security (since this fuel is used in military aircraft). Heretofore, JP-4 fuel has been eliminated from fuel supplies, due to proven fuel tank ullage volatility associated with its higher vapor pressures. The range of CO2-enriched fuels of the present invention, and the range of CO2 that can be absorbed within low, and very low vapor pressure fuels, make it possible to significantly increase jet fuel supply in times of emergency by providing the means to extend CO2-enriched Jet-A supplies by mixing in percentages of JP-4 or Naphthas (and increasing CO2 as needed), or increasing other usable jet fuel supplies by mixing suitable concentrations of CO2 in one or more non-Jet-A "JP" fuels. Such an approach can alternatively be employed in a non-crisis sitution, for instance where a government / country may be close to being self-sufficient in one or more fuel and could attain selfsufficiency by a prudent mixing of jet fuels and CO2.

The fact that carbon particulate is reduced in the engine exhaust means that any infra-red emissions from this source are also minimized. This can have value to military exhaust cloaking efforts.

Although the present invention has been described with a certain degree of particularity, it is understood that the present disclosure has been made by way of

example, and changes in detail or structure may be made without departing from the spirit of the invention as defined in the appended claims.